



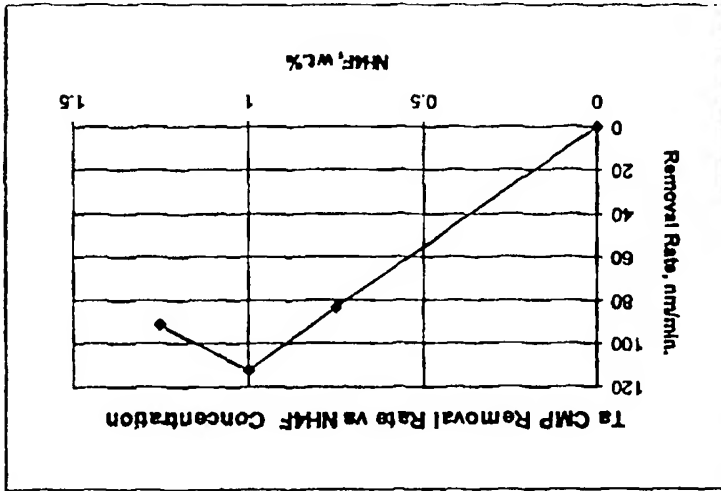
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(54) Title: COMPOSITION FOR THE CHEMICAL MECHANICAL POLISHING OF METAL LAYERS

(57) Abstract

A composition for CMP and a method for using the same, whereas the chemical mechanical polishing slurry composition comprises: a fluoride-containing compound, an abrasive and water. Optionally, an oxidizer and a carboxylic acid can be used as additives in the slurry composition. The resulting slurry is especially useful for the polishing of tantalum and copper layers on a substrate.



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## COMPOSITION FOR THE CHEMICAL MECHANICAL POLISHING OF METAL LAYERS

5 The present invention relates to the field of semiconductor integrated circuit manufacturing, and more particular to improved compositions for chemical mechanical polishing (CMP).

### BACKGROUND OF THE INVENTION

10 Recently copper has been introduced as the material for interconnecting the circuit elements on very large scale integrated circuit silicon wafers. Copper offers advantages over the currently-used tungsten because of its higher electrical conductivity and its resistance to electromigration. However, copper must be prevented from diffusing into the substrate upon which it has been deposited because trace levels of copper can interfere with the operation of the active circuit elements. Therefore, barrier layers are interposed between the copper and the underlying silicon or the underlying dielectric which is often silicon oxide. A favored barrier material in the industry is tantalum or tantalum nitride.

20 During the fabrication of these wafers, alternating layers of metal and dielectric are put on the silicon wafer by a variety of processes. After each layer is applied, a means is used to remove excess amounts of the layer and to assure both local and global planarity of the surface in preparation for the application of the next layer.

25 A common process used to accomplish these goals is chemical mechanical planarization or chemical mechanical polishing (CMP). In this process, an aqueous solution containing various chemicals and suspended abrasive particles, called a slurry, is interposed between the wafer and a moving pad while pressure is applied. The combination of the mechanical effects of the abrasive particles, applied pressure, imposed relative velocity and the chemical effects which result from

chemical reaction between the material being polished and constituents in the solution result in a synergistic enhancement of the polishing rate or material removal rate. That is, the material removal rate is higher than that produced by either the mechanical effects or chemical effects alone.

An interesting variant on the above scheme of CMP is available in which the abrasive particles are not suspended in the chemical solution. Rather, they are incorporated into the surface of the polishing pad. All subsequent comments regarding CMP are meant to pertain to both of these means of employing the abrasive particles.

In the case of CMP of metals, the chemical action is generally considered to take one of two forms. In the first mechanism, the chemicals in the solution react with the metal layer to continuously form an oxide layer on the surface of the metal. This generally requires the addition of an oxidizer to the solution such as hydrogen peroxide, ferric nitrate, etc. Thereafter, the mechanical abrasive action of the particles continuously and simultaneously removes this oxide layer. Optimum results in terms of removal rate and polished surface quality are obtained by a judicious balance of these two processes.

In the second mechanism, no protective oxide layer is formed. Instead, the constituents in the solution chemically attack and dissolve the metal, while the mechanical action is largely one of mechanically enhancing the dissolution rate by such processes as continuously exposing more surface area to chemical attack, raising the local temperature (which increases the dissolution rate) by the friction between the particles and the metal and enhancing the diffusion of reactants and products to and away from the surface by mixing and by reducing the thickness of the boundary layer.

In the case of CMP of the copper layers, experimental slurries are available from several manufacturers. These slurries generally give material removal rates of

from several hundred nanometers per minute to over one thousand nanometers per minute in pressure and relative velocity regimes typical of commercial CMP machines that are used in commercial water fabrication houses. Typical copper CMP slurries contain one or more carboxylic acids to lower the pH to below 7, and the abrasive particles used are typically alumina, silica, ceria or mixtures thereof.

5 There are also experimental copper polishing chemistries which are in the basic regime (pH greater than 7) which may be based on aqueous ammonia solutions, for example. The main drawback to these non-acid solutions is that the polishing rate of silica is also fairly high. One of the criteria for an acceptable metal layer polishing slurry is that the rate at which it removes the metal layer be much higher (by a factor of at least 20) than the rate at which it removes the dielectric layer (usually silicon oxide) under the metal layer.

10 In the CMP process for a metal layer, both the metal layer itself and its associated barrier layer or layers must be removed, leaving only the desired horizontal and vertical metal interconnects. In the case of copper CMP with a tantalum barrier layer, it is known that typical copper polishing slurries do not effectively remove the tantalum barrier layer at an acceptable rate. Since the Ta barrier layer is typically many times thinner than the copper layer, in order for it to be removed in an economically viable polishing time, the removal rate of the polishing system for the barrier layer need only be a fraction of that of the removal rate of the copper layer. The economically viable rate is defined by the fabricator of the wafers.

15 Unfortunately, tantalum exhibits the most stable passivity among known metals. This means that it is quite difficult to find a polishing solution that will overcome this passivity, which is due to the formation of a protective tantalum oxide film on the surface. For example, tantalum is resistant to attack by oxidizing metal chlorides, caustic alkali solutions, all the common inorganic acids and mixtures thereof such as aqua regia, as well as carboxylic acids which are used in copper polishing slurries (see, for example, H.H. Uhlig, "Corrosion and Corrosion

20 25 30

Control", John Wiley & Sons, 1967, pp 327-328 and M. Pourbaix, "Atlas of Electrochemical Equilibria in Aqueous Solutions", Pergamon Press, 1966, pp 251-255).

The reference by Uhlig indicates that Ta is attacked by hydrofluoric acid and fluorides in trace amounts. The reference by Pourbaix indicates that tantalum pentoxide (the passivating oxide) can be attacked by concentrated hydrofluoric acid. In order for a polishing solution to be commercially viable, however, it must not corrosively attack the polishing equipment which includes polishing machine parts and polishing pad. This essentially eliminates the possibility of using concentrated hydrofluoric acid as a CMP solution for tantalum.

### SUMMARY OF THE INVENTION.

The present invention describes a slurry composition for CMP and a method for using the same. The chemical mechanical polishing slurry composition comprises:

- (a) a fluorine-containing compound (e.g., fluoride-ion containing compound);
- (b) an abrasive; and
- (c) water.

Optionally, an oxidizer and a carboxylic acid can be used as additives in the slurry composition. The resulting slurry is especially useful for the polishing of tantalum and copper layers on a substrate.

### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph plotting Ta CMP removal rate versus  $\text{NH}_4\text{F}$  concentration; and

Fig. 2 is a graph plotting the effect of ammonium fluoride on copper CMP.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention consists of adding fluoride ions to a polishing

solution to enhance the removal rate of metal layers on integrated circuit silicon

wafers during CMP. One advantage of this approach is that it is effective at pH

values above 2 where corrosive attack of the polishing equipment is not a problem.

All of the examples below used ammonium fluoride as the source of fluoride ions,

but other fluorides could be used as well.

10 An advantage of the present invention is that the addition of fluoride ions

to certain copper polishing solutions does not seriously degrade the copper

polishing performance of the solution. Therefore, the potential exists of having

one polishing solution, either a slurry containing suspended abrasive particles or a

solution for use with a pad which has the abrasive particles incorporated within it,

15 that would effectively polish both the copper layer and its underlying tantalum

barrier layer.

The present invention is particularly directed to a chemical mechanical

polishing slurry composition comprising: (a) a fluoride-containing compound; (b)

20 an abrasive; and (c) water. The fluoride-containing compound is at least one

compound selected from the group consisting of: an acid fluoride; a fluorinated

salt; and a polyammonium fluoride salt. More particularly, the fluoride-containing

compound is at least one compound selected from the group consisting of:

hydrogen fluoride, perfluoric acid, alkali metal fluoride salt, alkaline earth metal

25 fluoride salt, ammonium fluoride, tetraethylammonium fluoride, ammonium

bifluoride, ethylenediammonium difluoride diethylenetriammonium trifluoride and

mixtures thereof. Most preferably, the fluoride-containing compound is

ammonium fluoride.

30 The composition according to the present invention may further comprise a  
carboxylic acid. Examples of suitable carboxylic acids are: formic acid, acetic

- acid, propanoic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid and mixtures thereof.
- The composition may also include an oxidizer. Suitable examples of oxidizers are hydrogen peroxide, potassium ferricyanide, potassium dichromate, potassium iodate, potassium bromate, vanadium trioxide, hypochlorous acid, sodium hypochlorite, potassium hypochlorite, calcium hypochlorite, magnesium hypochlorite, ferric nitrate, and mixtures thereof.
- 10 Other example of suitable oxidizers are ammonium persulfate, ammonium nitrate, potassium nitrate, potassium permanganate, ammonium hydroxide and mixtures thereof.
- 15 The pH of the composition is preferably between about 2 to 9, more preferably 2 to 7, and most preferably 3 to 4. The composition typically comprises between 0.01 to 2.0 molar fluoride ions, more preferably 0.14 to 0.41 molar fluoride ions, and most preferably 0.20 to 0.35 molar fluoride ions.
- 20 The abrasive is typically at least one abrasive selected from the group consisting of: silica, alumina, silicon carbide, silicon nitride, iron oxide, ceria and mixtures thereof. The composition typically comprises about 0.1 to 25% abrasive by weight.
- 25 The present invention also comprises a method for polishing which includes the steps of:
- (a) delivering a composition, wherein the composition comprises a fluorine-containing compound, an abrasive and water to a substrate;
- (b) contacting a polishing pad with the substrate and the composition; and
- (c) polishing the substrate with the composition.
- 30



Optionally, the abrasive is incorporated directly into the polishing pad.

This invention is explained below in further detail with references to

examples, which are not by way of limitation, but by way of illustration.

5

### Example 1

Example 1 shows the effectiveness of fluoride ions in the CMP of tantalum.

The results are summarized in Table 1 and Fig. 1. Aqueous solutions with

different concentrations of ammonium fluoride were used to polish tantalum

wafers with a diameter of 4 inches using a Struers KotoPol-3 laboratory polishing

machine, a Rodel IC 1000 perforated pad, a pressure of 3.8 psi, a relative velocity

between the pad and wafer of 236 feet per minute, and a solution flow rate of 40

ml/min. The abrasive particles were Ludox AM colloidal silica at a concentration

of 5 weight percent. No oxidizer was used in the slurry. Small amounts of

propanoic acid were added to assure that the pH remained in the range of 6.8-7.2.

Table 1 Ta Removal Rate.	
NH <sub>4</sub> F Conc. wt. %	RR, nm/min
0	0
0.75	83
1	112
1.25	91

If one considers a removal rate of 50 nm/min and above as acceptable, then

this slurry is effective for tantalum in a concentration range of about 0.5 weight

percent to at least 1.25 weight percent ammonium fluoride. This corresponds to a

molar concentration of fluoride ions of from 0.14 to 0.38 moles per liter. The

optimum is about 1 wt.% or 0.27 molar fluoride ion concentration.

In order to confirm that the beneficial effect was due to simultaneous chemical and mechanical action, the solution with 1 weight percent ammonium fluoride was used for polishing with no abrasive particles present. The removal rate due to chemical action alone was 8 nm/min. The first data point in Table 1 shows that mechanical action without the presence of ammonium fluoride results in a removal rate of essentially zero. In contrast, when both chemical and mechanical activity are present simultaneously, the removal rate (data point #3 in Table 1) was 112 nm/min. Thus, the synergistic effect of chemical and mechanical action is confirmed.

### Example 2

Another example of the effectiveness of this invention is shown in Table 2. The polishing conditions and abrasive content were the same as in Table 1. In this case, however, the propanoic acid concentration was increased substantially to reduce the pH to 3.9, a value more typical of CMP of many metals such as copper. Also, the effect of oxidizer concentration was investigated at two levels.

Lowering the pH at a fixed concentration of 1 weight percent ammonium fluoride increased the removal rate by about 50 percent from 112 nm/min to 179 nm/min, all with no intentional oxidizer added (compare data point #3 in Table 1 with data point #1 in Table 2). Table 2 shows that adding oxidizer in the form of 7.5 volume percent hydrogen peroxide reduced the removal rate by about 25 percent. However, the removal rates of both slurries in Table 2 are acceptable.

Tantalum Removal Rates in Propanoic Acid Solutions with 1 Weight Percent Ammonium Fluoride, pH = 3.9			
Acid Conc. moles/liter	Hydrogen Peroxide conc. nm/min.	Removal Rate,	
		vol. %	
1.3	0	179	

**Example 3**

Example 3 shows that this basic chemistry provides an acceptable tantalum

removal rate when the abrasive particles are incorporated into the polishing pad rather than suspended in the solution as in the following. The abrasive particles in this case were alumina rather than the colloidal silica particles in the examples

previously cited. A 1 weight percent ammonium fluoride aqueous solution with a pH of 7.1 was used to polish a tantalum water at a pressure of 8.9 psi. and a

relative velocity of 236 ft/min. The average removal rate was 70 nm/min. This is somewhat less than the 112 nm/min. obtained at the same  $\text{NH}_4\text{F}$  concentration in

Table 1 and required a higher pressure. However, the polishing performance of the abrasive-impregnated pad has been found to be highly dependent on the resilience of the backing used for the pad. Therefore, this example merely shows that the same basic chemistry works effectively regardless of whether the particles are

suspended in the solution or embedded in the polishing pad.

**Example 4**

Example 4 shows the effectiveness of the basic chemistry used to polish

copper wafers. The results are shown in Table 3 and Fig. 2. The polishing

pressures and relative velocities were the same as in Table 1. However, in the present slurries, the concentration of colloidal silica was only 2.5 weight percent instead of 5 weight percent. In addition, an oxidizer content of 6.5 volume percent hydrogen peroxide was used to enhance the copper polishing rate.

Table 3 Effect of $\text{NH}_4\text{F}$ on Copper CMP Removal Rates, nm/min			
Composition	Wt.% $\text{NH}_4\text{F}$	Molar Propanoic Acid	Polishing Rate
1	0	0 (pH=3.8)	-
2	0.25	0 (pH=3.8)	680

3	0.5	0 (pH = 3.8)	650
4	0	0.88 (pH=3.5-3.6)	1120
5	0.1	0.88 (pH=3.5-3.6)	870
6	0.1	0.88 (pH=3.5-3.6)	1120
7	0.15	0.88 (pH=3.5-3.6)	960
8	1.0	1.4-1.4 (pH=3.8)	590
9	1.5	1.4-1.5 (pH=3.8)	430

Table 3 and Fig. 2 show that the addition of ammonium fluoride to a slurry does not significantly degrade the polishing rate of copper. In fact, the polishing rate is enhanced by ammonium fluoride additions. This is similar to the effect observed in the tantalum examples discussed above. For comparison, the removal rate of a fluoride-free commercial slurry from Rodel was found to be about 1120 nm/min under identical polishing conditions.

#### Example 5

This example shows the beneficial effect of fluoride ions on the CMP of tungsten. The results are summarized in Table 4 below. The polishing slurries contained 4.7 weight percent fumed silica from Wacker, a hydrogen peroxide concentration of 7 volume percent and were polished at a pressure of 7.6 psi and a relative velocity of 236 fpm. The pH was 4.7 to 5.0. Adding the ammonium fluoride essentially tripled the removal rate.

Table 4			
Effect of NH <sub>4</sub> F on W CMP		Weight %	NH <sub>4</sub> F
		Removal Rate,	nm/min.
0	177		
1	563		

For polishing slurries to be commercially viable, they must meet two other criteria besides having an adequate removal rate and leaving an acceptable surface finish. These are that the polishing rate of silica must be acceptably low and that the static etch rate (the removal rate when no pressure or relative velocity is applied and no particles are present) of both silica and the metal in the solution must be acceptably low.

We have already seen above that the static etch rate of tantalum in a 1 weight percent ammonium fluoride solution at pH 6.8 - 7.2 was only 8 nm/min.

The static etch rate of copper in a 0.9 M propanoic acid solution with a pH of 3.9, a hydrogen peroxide concentration of 7.5 volume percent and 1 weight percent ammonium fluoride was 35 nm/min. This is about 17 times lower than the polishing rate for such a solution that contains 2.5 weight percent colloidal silica.

The static etch rate of tungsten in solutions with a pH of 3.5 to 4, 7.5 volume percent hydrogen peroxide and up to 2 weight percent ammonium fluoride was less than 10 nm/min.

We have found that solutions containing 0.9 molar propanoic acid with a pH of about 3.5 and 6.5 to 7.5 volume percent hydrogen peroxide show a static etch rate of essentially zero in solutions containing up to 1 weight percent ammonium fluoride. In such solutions containing up to 0.15 weight percent ammonium fluoride and 2.5 weight percent colloidal silica particles, the polishing rate varied from about 7 nm/min to about 14 nm/min at 3.8 psi pressure and 236 ft./min. relative velocity.

It has therefore been demonstrated that aqueous solutions containing abrasive particles either suspended in the solution or incorporated in the polishing pad and up to about 0.6 moles per liter of fluoride ion, at pH values in the range of 2 to 7, are effective in the chemical mechanical polishing of tantalum, copper and

tungsten. In the case of tantalum CMP, the optimum fluoride concentration is about 0.27 molar. In addition, it has been demonstrated that propanoic acid enhances the polishing rate of these metals in such solutions.

5 While the invention has been described in combination with embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications and variations as fall within the spirit and broad scope of the appended claims.

10

**What is claimed is:**

1. A chemical mechanical polishing slurry composition comprising:

(a) a fluoride-containing compound;

(b) an abrasive; and

(c) water.

5

2. The composition of claim 1 wherein said fluoride-containing

compound is at least one compound selected from the group consisting of:

(a) an acid fluoride;

(b) a fluorinated salt; and

(c) a polyammonium fluoride salt.

10

3. The composition of claim 1 wherein said fluoride-containing

compound is at least one compound selected from the group consisting of:

hydrogen fluoride, perfluoric acid, alkali metal fluoride salt, alkaline earth metal

fluoride salt, ammonium fluoride, tetramethylammonium fluoride, ammonium

bifluoride, ethylenediammonium difluoride, diethylenetriammonium trifluoride and

mixtures thereof.

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4. The composition of claim 3 wherein said fluoride-containing

compound is ammonium fluoride.

5. The composition of claim 1 wherein said abrasive is at least one

abrasive selected from the group consisting of: silica, alumina, silicon carbide,

silicon nitride, iron oxide, ceria and mixtures thereof.

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6. The composition of claim 1 further comprising a carboxylic acid.

7. The composition of claim 6 wherein said carboxylic acid is at least

one acid selected from the group consisting of: formic acid, acetic acid, propanoic

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acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid and mixtures thereof.

8. The composition of claim 1 further comprising an oxidizer.

9. The composition of claim 8 wherein said oxidizer is at least one compound selected from the group consisting of: hydrogen peroxide, potassium ferricyanide, potassium dichromate, potassium iodate, potassium bromate, vanadium trioxide, hypochlorous acid, sodium hypochlorite, potassium hypochlorite, calcium hypochlorite, magnesium hypochlorite, ferric nitrate, ammonium persulfate, ammonium nitrate, potassium nitrate, potassium permanganate, ammonium hydroxide and mixtures thereof.

10. The composition of claim 1 wherein the pH of said composition is between about 2 to 9.

11. The composition of claim 10 wherein the pH of said composition is between about 2 to 7.

12. The composition of claim 11 wherein the pH of said composition is between about 3 to 4.

13. The composition of claim 1 wherein said composition has a concentration of fluoride ions between about 0.01 to 2.0 molar.

14. The composition of claim 1 wherein said composition has a concentration of fluoride ions between about 0.14 to 0.41 molar.

15. The composition of claim 1 wherein said composition has a concentration of fluoride ions between about 0.20 to 3.35 molar.



16. The composition of claim 1 wherein said composition comprises about 0.1 to 25% abrasive by weight based upon the total weight of said composition

5 17. A method for polishing comprising the steps of:

- (a) delivering a composition, wherein said composition comprises a fluorine-containing compound, an abrasive and water, to a substrate;
- (b) contacting a polishing pad with said substrate and said composition; and
- (c) polishing said substrate with said composition.

18. The method of claim 17 wherein said fluorine-containing compound is at least one compound selected from the group consisting of:

- (a) an acid fluoride;
- (b) a fluorinated salt; and
- (c) a polyammonium fluoride salt.

19. The method of claim 18 wherein said fluorine-containing compound is at least one compound selected from the group consisting of: hydrogen fluoride, perfluoric acid, alkali metal fluoride salt, alkaline earth metal fluoride salt, ammonium fluoride, tetramethylammonium fluoride, ammonium bifluoride, ethylenediammonium difluoride, diethylenetriammonium trifluoride and mixtures thereof.

20. The method of claim 19 wherein said fluorine-containing compound is ammonium fluoride.

21. The method of claim 17 wherein said abrasive is at least one abrasive selected from the group consisting of: silica, alumina, silicon carbide, silicon nitride, iron oxide, ceria and mixtures thereof.

22. The method of claim 17 wherein said substrate comprises an overcoat layer selected from the group consisting of: tantalum, titanium-tungsten, tungsten, copper, aluminum, and their nitrides, silicides, carbides and oxides thereof.

23. The method of claim 17 wherein said composition further comprises a carboxylic acid.

24. The method of claim 23 wherein said carboxylic acid is at least one acid selected from the group consisting of: formic acid, acetic acid, propanoic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid and mixtures thereof.

25. The method of claim 17 wherein said composition further comprising an oxidizer.

26. The method of claim 25 wherein the oxidizer is at least one selected from the group consisting of: hydrogen peroxide, potassium ferricyanide, potassium dichromate, potassium iodate, potassium bromate, vanadium trioxide, hypochlorous acid, sodium hypochlorite, potassium hypochlorite, calcium hypochlorite, magnesium hypochlorite, ferric nitrate, ammonium persulfate, ammonium nitrate, potassium nitrate, potassium permanganate, ammonium hydroxide and mixtures thereof.

27. The method of claim 17 wherein said composition has a pH between about 2 to 9.

28. The method of claim 27 wherein said composition has a pH between about 2 to 7.

29. The method of claim 28 wherein said composition has a pH between about 3 to 4.

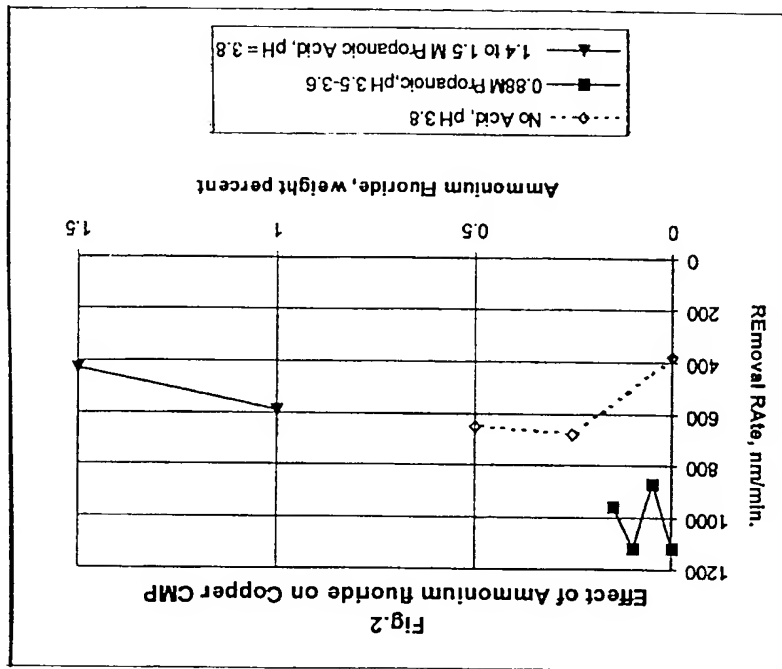
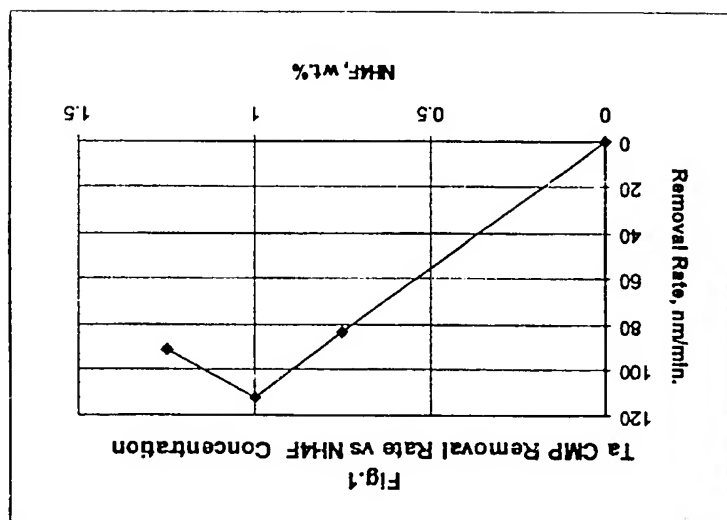
30. The method of claim 17 wherein said composition has a concentration of fluoride ions between about 0.01 to 2.0 molar.

31. The method of claim 30 wherein said composition has a concentration of fluoride ions between about 0.14 to 0.41 molar.

32. The method of claim 31 wherein said composition has a concentration of fluoride ions between about 0.20 to 0.35 molar.

33. The method of claim 17 wherein said composition comprises between about 0.1 to 25% abrasive by weight based upon the total weight of said composition.

34. The method of claim 17 wherein said abrasive is incorporated directly into said polishing pad.



# INTERNATIONAL SEARCH REPORT

International application No. PCT/US99/13709

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B24B 37/04; C23F 1/44; H01L 21/302  
US CL : 451/41; 51/308; 438/691  
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 451/41; 51/308; 438/691; 692; 693; 252/79.4

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,516,346 A (Cadien et al) 14 May 1996, col. 10-11.	1-16
Y,P	US 5,836,806 A (Cadien et al) 17 November 1998, col. 10-12.	17-34
Y	US 5,700,383 A (Feller et al) 23 December 1997, col. 7-10.	1-16
T	US 5,934,980 A (Koos et al) 10 August 1999, col. 6-7.	4, 8, 9, 20, 25, 26

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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